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LETTERS TO THE EDITOR

Adsorption equations for active carbons with inhomogeneous microporous structures

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The widest popularity in describing the Physical adsorption of gases and vapors in micropores is enjoyed by the theory of volume filling of micropores. The general equation of the theory can be presented in the form (1) proposed by Dubinin and Astakhov[1]:

$$W = W_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \tag{1}$$

where

$$A = RT \ln (p_s/p)] \tag{2}$$

or in the form of the Dubinin–Radushkevich equation for $n = 2$[1]:

$$W = W_0 \exp\left[-B\frac{T^2}{\beta^2}\log^2 (p_s/p)\right] \tag{3}$$

or else in shorter formulation:

$$W = W_0 \exp[-By] \tag{4}$$

where

$$y = \left[\frac{T}{\beta}\log (p_s/p)\right]^2. \tag{5}$$

At $n = 2$ the relationship between the principal parameters E_0 and B of eqns (1) and (3) or (1) and (4), which are essentially identical, is expressed by

$$E_0 = 19.15\sqrt{[1/(B \times 10^6)]}. \tag{6}$$

Equation (1) for $n = 2$ and eqn (3) are applicable over wide ranges of equilibrium relative pressures for microporous carbonaceous adsorbents or active carbons with a relatively narrow micropore size distribution. The microporous structures of such active carbons can, somewhat conventionally, be considered homogeneous.

At high degrees of activation, however, the walls between adjacent micropores burn out gradually with the resulting formation of supermicropores, a larger variety of micropores. Assuming that adsorption in micro- and supermicropores occurs independently, it is possible to write, to a good approximation, the following adsorption equation for = 2 in the form (1)

$$W = W_{01}\exp\left[-\left(\frac{A}{\beta E_{01}}\right)^2\right] + W_{02}\exp\left[-\left(\frac{A}{\beta E_{02}}\right)^2\right] \tag{7}$$

for such active carbons with a wide micropore distribution. The parameters of this equation are micropore volume the characteristic adsorption energy E_{01} of the standard vapor in the micropores, and W_{02} and E_{02} the respective values for the supermicropores.

Kadlec[2] and then Rand[3] showed that the adsorption equation (1) with a nonintegral value of parameter n less than 2 and more than 1 could be used for such carbons. Such an equation contains three parameters W_0, E_0 and n.

Stoeckli made an attempt to generalize the Dubinin-Radushkevich equation (4) for active carbons with a wide micropore distribution at a constant integral value $n = 2$ as in eqn (7)[4, 5]. By analogy with this equation we can write for a continuous distribution, when volume W_{0i} becomes a function of parameter B:

$$W = \int_0^\infty f(B)\exp[-By]\,dB. \tag{8}$$

Stoeckli's principal idea was to apply the normal Gaussian distribution (9) to $f(B)$

$$f(B) = \frac{W_0}{\Delta\sqrt{(2\pi)}}\exp\left[-\frac{(B_0 - B)^2}{2\Delta^2}\right]. \tag{9}$$

As a result, the adsorption equation (10) obtained by Stoeckli contained three parameters W_0, B_0 and dispersion Δ[4, 5]:

$$W = W_0 \exp[-B_0 y]\exp\left[\frac{y^2\Delta^2}{2}\right]0.5[1 - \text{erf}(z)] \tag{10}$$

where

$$z = \left(y - \frac{B_0}{\Delta^2}\right)\frac{\Delta}{\sqrt{2}}. \tag{11}$$

In principle, the Stoeckli equation (10) is more rigorous than Dubinin's two-term eqn (7). Both equations, however, yield practically identical results with a high degree of accuracy. An example is Table 1 generalizing, in the form of the corresponding isotherm of adsorption of the standard vapour—benzene—the experimental data on equilibrium adsorption of six different vapors at different temperatures[5, 6]. The advantage of eqn (7) lies in the possibility of classification the micropores into two varieties, i.e. micropores proper and supermicropores, and estimating their parameters.

As already noted, a wide micropore distribution can be described by eqn (1) with a nonintegral value of parameter n less than 2 and more than 1. We have shown that in this case the value of parameter n is directly related to dispersion Δ by a linear dependence.

Table 1.

		W cm³/g		
$y \times 10^6$	p/p_s	Experiment (average)	Calculated by Stoeckli	Calculated according to TVFM
8.00	2.25×10^{-10}	0.0020	0.0024	0.0020
4.00	1.50×10^{-7}	0.020	0.020	0.023
2.00	1.30×10^{-5}	0.093	0.097	0.102
1.00	3.89×10^{-4}	0.244	0.238	0.228
0.50	3.87×10^{-3}	0.395	0.386	0.391
0.10	8.30×10^{-2}	0.581	0.577	0.579
0.05	1.73×10^{-1}	0.610	0.608	0.609

Table 2.

Active carbon	Experiment, calculated by eqn (1) W_0 cm³/g	$B_0 \times 10^6$	$\Delta \times 10^6$	Experiment by (1) n	Calculated by (12) n	Divergence %
U-02	0.43	0.92	0.21	1.65	1.60	−3.0
F-02	0.64	1.03	0.29	1.47	1.45	−2.5
F-85	0.75	0.98	0.35	1.28	1.33	4.2
T	0.40	0.61	0	2.00	2.00	0
Carbosieve	0.51	0.57	0	2.00	2.00	0
AC-400 de-ashed	0.42	0.61	0.15	1.71	1.71	0
AC-900 de-ashed	0.41	0.70	0.14	1.70	1.73	2.0

$$n = 2.00 - 1.90 \times 10^6 \Delta. \quad (12)$$

The results of experiments by Stoeckli and Houriet [5, 6] serve as a vivid illustration (Table 2 and Fig. 1). Thus a physical meaning can be attributed to a parameter n equal to two for micropores of different sizes. The indicated nonintegral values of n are effective values directly associated with dispersion Δ, which characterizes the distribution width.

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Adsorption of acetaldehyde and ethane on activated carbon

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We used a dynamical method to determine the volume adsorption capacity at 25°C of Columbia type 4LXC 12/28 activated carbon for acetaldehyde and ethane at low partial pressures in a helium carrier gas. The experimental apparatus was described previously [1]. The gas flowed through the adsorber bed at a constant rate with fluctuations of less than 1%. The flow rate was 200 cc(STP)/min in the acetaldehyde experiments and 50 cc(STP)/min in the ethane experiments. The (10 cm long, 0.454 cm inside diameter) cylindrical adsorber bed in the acetaldehyde experiments was packed with 0.569 g of carbon. The carbon mass was determined after 48 hr of desorption at 200°C. The (40 cm long, 0.486 cm inside diameter) adsorber bed in the ethane experiments was packed with 2.638 g of carbon. After each adsorption experiment, the adsorber bed was cleaned by raising the temperature to 150°C and purging with high-purity helium for more than 6 hr.

The pressure drop across the adsorber bed was 17 Torr in the acetaldehyde experiments and 6 Torr in the ethane experiments, while the total pressure ranged from 760 to 780 Torr. The partial pressures varied from 4 to 80 millitorr in the acetaldehyde experiments and from 20 to 400 millitorr in the ethane experiments. The temperature of the adsorber bed in all experiments was controlled at (25 ± 0.02)°C. We measured the concentration at the outlet to the bed within 1%. Numerical integration of the resulting concentration-vs-time curve yielded the volume adsorption capacity K [cc(STP)/g]. The experimental procedures were described previously [2]. The volume adsorption capacity data were fitted to the Freundlich isotherm equation, viz.

$$K = kp^{1/n} \quad (1)$$

where p (Torr) is the partial pressure. The least-squares values of the parameters k and n are 23.02 and 1.34 for acetaldehyde; and 2.20 and 1.06 for ethane. The corresponding standard deviations in the fits are 0.016 and 0.009, respectively. The fact that n for ethane is very close to unity signifies that the adsorption isotherm for ethane does not deviate substantially from Henry's law for the range of pressures studied here. Also, it should be mentioned that the adsorption capacity data cannot be interpreted in

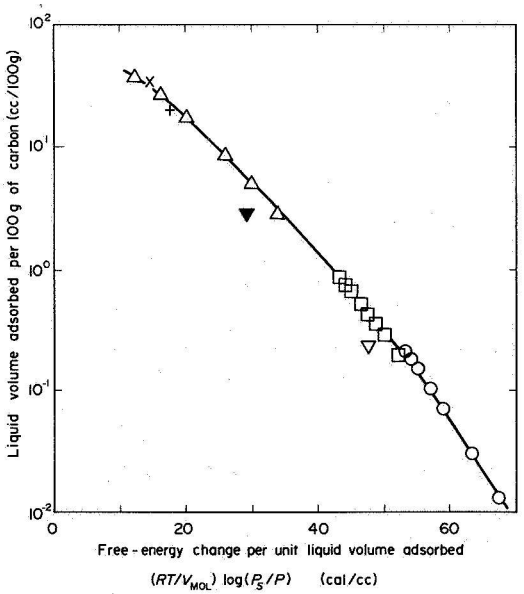

Fig. 1. Generalised correlation diagram for Columbia 4LXC 12/28 activated carbon. Symbols: △ acetone, □ acetaldehyde, ○ ethane, × toluene, + freon-113, ▼ ethanol, ▽ methanol.

terms of the monolayer Langmuir equation (in spite of the apparently good fit) since the relation between K^{-1} and p^{-1} is not linear.

Following Lewis *et al.*[3] we plotted the liquid volume adsorbed per unit mass of carbon vs the isothermal free-energy change in passing from the liquid state to the adsorbed state per unit liquid volume adsorbed for acetaldehyde and ethane. The resulting generalized correlation diagram is shown in Fig. 1. To extend the correlation diagram to the high adsorption region, we used adsorption capacity data obtained by Madey *et al.*† for acetone on the same type of carbon at 25°C. Included on this diagram are points corresponding to the adsorption of freon-113 and ethanol[1] and also toluene and methanol[4] on the same type of carbon at 25°C. We note that the values for the two alcohols do not fall on the same correlation curve with the other compounds. Since the pressures investigated are much smaller than the corresponding critical pressure for each compound ($p/p_c < 2 \times 10^{-4}$), we used the pressures rather than the fugacities in the correlation diagram. The liquid molar volumes and the vapor pressures were obtained from Ref. [5].

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Mesophase formation from decacyclene

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Since the first report of carbonaceous mesophase by Brooks and Taylor[1], a large number of studies have been made on this subject, e.g. the nucleation, growth and coalescence processes of mesophase spherules and their behaviour in a magnetic field[2–4]. Most of the studies have confirmed the findings of Brooks and Taylor that in the individual mesophase spherule flat aromatic molecules lie parallel to each other in the interior and perpendicular to the surface of the spherule near the surface. Recently two different types of mesophase spherules have been reported by Imamura *et al.* and Kovac *et al.*[7]: The first spherule has a dish-like structure, which has been found both in a coal tar pitch containing small amounts of carbon black[5] and synthetic pitches made from anthracene and naphthalene with $AlCl_3$[7]. The second spherule has been obtained from both a coal tar pitch and Khafji asphalt heat-treated at temperatures below 370°C[6]. These spherules have different optical properties from those of the above Brooks-Taylor spherules. In addition to these, another type of spherule has now been found for pitches from decacyclene. The object of the present letter is to describe some optical observations of mesophase spherules with unusual optical properties and to propose a possible structural model.

Decacyclene ($C_{36}H_{18}$) was supplied from ICN-K&K laboratories Inc. and used without purification. Carbonization was carried out at 350–650°C in a test tube under nitrogen atmosphere with a heating rate of 100°C/hr. A Leitz reflected light microscope was used to examine the optical structures of the pyrolysis residues. Solvent fractionation was carried out with benzene and quinoline to characterize the residues obtained under various conditions.

Decacyclene is produced abundantly as one of the main products in acenaphthylene pitch pyrolysed at temperatures between 320 and 470°C[8, 9]. Decacyclene yields pitch-like materials at about 530°C and coke at about 570°C when heat-treated. The temperature range over which the carbonization reactions proceed in the liquid phase was found to be narrow, only 40°C (530–570°C). Microphotographs of the pyrolysis residues from decacyclene are shown in Fig. 1. Up to 540°C crystalline materials with a strong optical anisotropy were observed over the entire region of the residue. These materials have been also found when acenaphthylene was heat-treated between 320 and 470°C. With increasing heat treatment temperature (HTT), the crystalline materials become small in size, and then mesophase of irregular shape appears at 540°C. Mesophase spherules of 30–100 μm diameter are observed in the residue heat-treated at 550°C, as shown in Fig. 1, although small crystalline materials are still present in the pitch matrix. All the mesophase spherules in this case have a maltese cross and are distinct from the Brooks-Taylor ones. At above 560°C, these spherules coalesce to yield

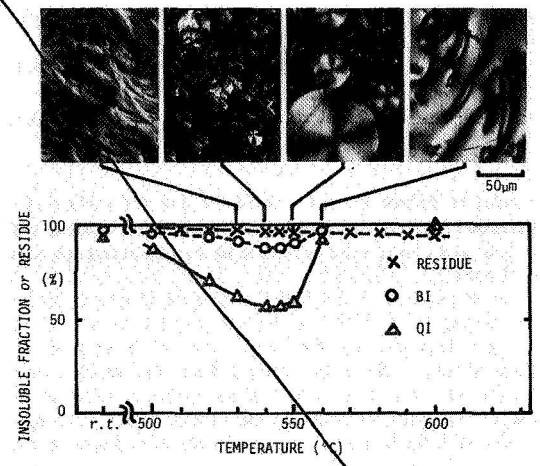

Fig. 1. Optical micrographs (crossed nicols) of decacyclene heat-treated at 530–560°C, and variations in the yields of pyrolysis residue, benzene- and quinoline-insoluble fractions with heat treatment temperature.

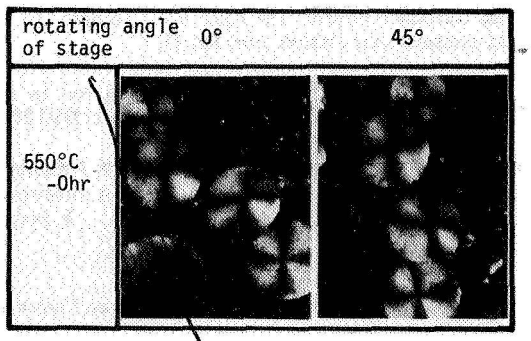

Fig. 2. Carbonaceous mesophase spherules from decacyclene at HTT 550°C (crossed nicols).

bulk mesophase with a fibrous texture in the same manner as acenaphthylene pitch.

In Fig. 1 are also shown the yields of benzene and quinoline insoluble fractions (BI and QI) of the pyrolysis residues. Pure decacyclene is sparingly soluble in benzene and quinoline. The residue heat-treated at 500°C becomes partly soluble in both benzene and quinoline and a maximum solubility was found for the residue heat-treated around 540°C. At HTT 560°C, the pyrolysis residue is almost insoluble in benzene and quinoline.

All the mesophase spherules from decacyclene show a maltese cross which remains unchanged with stage rotation as shown in Fig. 2. A mesophase spherule with a maltese cross is occasionally observed in the pyrolysis residues of acenaphthylene and coal tar pitch, which yield normal Brooks–Taylor spherules, if the cut section of a spherule is perpendicular to the polar axis. In the case of decacyclene pitch, however, all the spherules have a maltese cross as if they were obtained under the influence of a magnetic field. Therefore, it can be concluded that the mesophase spherules from decacyclene pitch have a structure different from that of the Brooks–Taylor ones. We propose a structural model for the spherules obtained from decacyclene pitch as shown in Fig. 3. In this model all layers lie in concentric circles around the center of the spherule.

From these observations we conclude as follows:

(1) The temperature range over which the carbonization reactions of decacyclene proceed in the liquid phase is very narrow, only 40°C (from 530 to 570°C) when a heating rate was 100°C/hr.

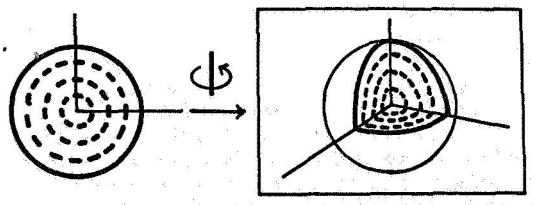

Fig. 3. A structural model for the mesophase spherules from decacyclene.

(2) All the mesophase spherules from decacyclene pitch show a maltese cross which remains unchanged with the stage rotation of a microscope.

(3) A structural model is proposed, in which all the layers in a spherule lie in concentric circles around the center of the spherule.

(4) Those mesophase spherules with a maltese cross coalesce to yield bulk mesophase with fibrous textures like acenaphthylene pitch.

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Evolution of ethylene and acetylene from ethane-treated diamond powders

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In order to deduce the structure of the diamond surface after interaction with hydrocarbons, diamond powders treated with methane and ethane were submitted to thermal-desorption mass spectrometry[1]. Diamond powders heated in a methane or ethane atmosphere at 400–1100°C evolved hydrogen molecules on reheating up to 1250°C under vacuum; the amount of the hydrogen depended on the temperature of heating in the hydrocarbons[2]. Since the cooling from the reaction temperature was very rapid, a part of the hydrogen atoms of the hydrocarbons must be bound to the surface carbon atom upon reaction with the hydrocarbons. In addition to hydrogen, evolution of slight amounts of ethylene and acetylene was observed for the samples heated in ethane.

After outgassing up to 1150°C at 10^{-6} Torr, natural diamond powders (0–0.5μm) were heated in 10^{-2} Torr ethane at 400–700°C for 1 hr and then cooled rapidly. On reheating at 10^{-7} Torr at a rate of 18°C/min, gases with *m/e* values of 25, 26, 27 and 28 desorbed at the initial stage of gas evolution (400–700°C). Figure 1(a) shows a typical mass spectrum. The comparison of the spectrum with the patterns of ethane, ethylene and acetylene (Fig. 2) indicates that the evolved gases are ethylene and acetylene. The total amounts of ethylene and acetylene evolved were three orders of magnitude smaller than the amount of the desorbed hydrogen. The evolution of ethane was not clear because of the simultaneous desorption of carbon monoxide which resulted from the reactions of oxygen and water with diamond surface during the ethane-treatment. In contrast, neither methane nor higher hydrocarbons were evolved to a detectable degree in similar experiments with methane.

The evolution of ethylene and acetylene may be explained in terms of the following process: both CH_3CH_2- and $-CH_2CH_2-$ groups are formed on the diamond surface as a result of ethane-